

interference search for 10/500,542

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	491	(556/11).CCLS.	US-PGPUB; USPAT; EPO; JPO	OR	OFF	2005/09/19 10:56
L2	519	(556/12).CCLS.	US-PGPUB; USPAT; EPO; JPO	OR	OFF	2005/09/19 11:16
L3	1017	(534/15).CCLS.	US-PGPUB; USPAT; EPO; JPO	OR	OFF	2005/09/19 11:16

10/500,542

(FILE 'HOME' ENTERED AT 12:00:07 ON 19 SEP 2005)

FILE 'REGISTRY' ENTERED AT 12:00:19 ON 19 SEP 2005

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR

Structure diagram not available for display

Structure attributes must be viewed using STN Express query preparation.

=> s l1

SAMPLE SEARCH INITIATED 12:00:45 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 430 TO ITERATE

100.0% PROCESSED 430 ITERATIONS

50 ANSWERS

INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**

BATCH **COMPLETE**

PROJECTED ITERATIONS: 7356 TO 9844

PROJECTED ANSWERS: 3385 TO 5135

L2 50 SEA SSS SAM L1

=> s l1 full

FULL SEARCH INITIATED 12:00:51 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 8215 TO ITERATE

100.0% PROCESSED 8215 ITERATIONS

4148 ANSWERS

SEARCH TIME: 00.00.01

L3 4148 SEA SSS FUL L1

=> fil caplus

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

161.33

161.54

FILE 'CAPLUS' ENTERED AT 12:00:56 ON 19 SEP 2005

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

COPYRIGHT (C) 2005 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December 26, 1996), unless otherwise indicated in the original publications. The CA Lexicon is the copyrighted intellectual property of the American Chemical Society and is provided to assist you in searching databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS 1907 - 19 Sep 2005 VOL 143 ISS 13

FILE LAST UPDATED: 18 Sep 2005 (20050918/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s l3/prep
 2864 L3
 3358361 PREP/RL
 L4 1036 L3/PREP
 (L3 (L) PREP/RL)

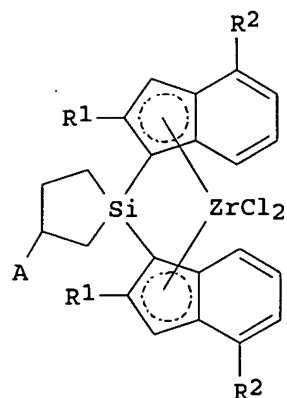
=> s l4 and py<2002
 21803847 PY<2002
 L5 680 L4 AND PY<2002

=> s l5 and alkylation
 93944 ALKYLATION
 L6 27 L5 AND ALKYLATION

=> d 1-27 bib abs

L6 ANSWER 1 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
 AN 2002:421732 CAPLUS
 DN 136:386261
 TI Ansa-zirconocenes functionalized on their cyclosilane bridges, their
 preparation and activity as polymerization catalysts
 IN Lemenovskii, D. A.; Krut'ko, D. P.; Borzov, M. V.; Brusova, G. P.;
 Veksler, E. N.; Nedorezova, P. M.; Tsvetkova, V. I.
 PA Institut Khimicheskoi Fiziki RAN im. N. N. Semenova, Russia
 SO Russ., No pp. given
 CODEN: RUXXE7
 DT Patent
 LA Russian
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	RU 2160277	C1	20001210	RU 1999-113532	19990621 <--
PRAI	RU 1999-113532		19990621		
OS	CASREACT 136:386261; MARPAT 136:386261				
GI					



AB Ansa-zirconocenes functionalized on their cyclosilane bridges I [R1 = H, Me, Et; R2 = H, (un)branched C1-4 alkyl, aryl; A = BC8H14, MR3; M = Sn, Si; R = (un)branched C1-4 alkyl, aryl], useful as catalysts for preparation of polyolefins, are claimed. Also claimed is a method for preparation of I comprising synthesizing substituted indene, preparing the Li salt of the indene and reaction of the latter with 1,1-dichloro-2,5-dihydrosilole in Et2O and subsequently treating the resulting dilithium salt of the corresponding Si-bridged bis-indenyl ligand with ZrCl4 to give the corresponding zirconocene and heating it in THF with an alkyl(aryl)derivative of B monohydride, Sn or Si. This method makes it possible to obtain high yields of intermediates and desired products and permits increasing content of active racemic form in metallic complex. The resulting compds. have high catalytic activity and stereoselectivity in the polymerization of propylene. In an example, reaction of indenyllithium with 1,1-dichloro-2,5-dihydrosilole gave the bis(indenyl)silole bidentate

ligand which formed a dilithium salt-Et₂O adduct upon treatment with BuLi in Et₂O, and complexation of the latter with ZrCl₄ in PhMe and subsequent functionalization with 9-BBN in THF gave I (R₁ = R₂ = H, AH = 9-BBN), and its catalytic activity for polymerization of propylene was demonstrated.

L6 ANSWER 2 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 2002:416502 CAPLUS
DN 136:386260

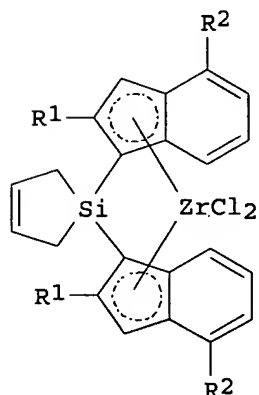
TI Ansa-zirconocenes with an unsaturated cyclosilane bridge, their preparation and activity as polymerization catalysts
IN Lemenovskii, D. A.; Avtomonov, E. V.; Krut'ko, D. P.; Borzov, M. V.; Kazennova, N. B.; Tsvetkova, V. I.; Nedorezova, P. M.; Aladyshev, A. M.; Savinov, D. V.

PA Institut Khimicheskoi Fiziki im. N. N. Semenova RAN, Russia
SO Russ., No pp. given
CODEN: RUXXE7

DT Patent
LA Russian

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	RU 2160276	C1	20001210	RU 1999-113531	19990621 <--
PRAI	RU 1999-113531		19990621		
OS	CASREACT 136:386260; MARPAT 136:386260				
GI					



I

AB Ansa-zirconocenes having an unsatd. cyclosilane bridge I (R₁ = H, Me, Et; R₂ = H, (un)branched C1-4 alkyl, aryl), useful as polymerization catalysts for polyolefin preparation, are claimed. Also claimed is a method for preparation of I by reaction of a lithium derivative of indene with 1,1-dichloro-2,5-dihydrosilole in Et₂O to give a bis-indenyl ligand having a cyclosilane bridge; subsequent dilithiation of the bis-indenyl ligand thus obtained affords a salt which exists as a crystalline adduct of Et₂O, which upon treatment with ZrCl₄ affords the desired product with high yield. Compds. I have high catalytic activity and stereoselectivity in polymerization reactions as mixts. of rac (active) and meso (inactive) forms. In an example, lithiation of 2-ethyl-4-phenylindene (preparation given) with BuLi and subsequent silylation with 1,1-dichloro-2,5-dihydrosilole gave nearly quant. the bidentate ligand 1,1-bis(2-ethyl-4-phenyl-1-yl)-2,5-dihydrosilole which formed 70% of a crystalline salt-Et₂O adduct upon dilithiation; treating the latter with ZrCl₄ in PhMe gave 67% I (R₁ = Et, R₂ = Ph) as a 2:1 mixture of rac and meso isomers, and these demonstrated improved catalytic activity in the polymerization of propylene over known zirconocene catalysts.

L6 ANSWER 3 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 2000:425914 CAPLUS
DN 133:164142

TI Synthesis and Structure of a Hypercoordinate Silicon-Bridged

[1]Ferrocenophane
 AU Jaekle, Frieder; Vejzovic, Emira; Power-Billard, K. Nicole; MacLachlan,
 Mark J.; Lough, Alan J.; Manners, Ian
 CS Department of Chemistry, University of Toronto, Toronto, ON, M5S 3H6, Can.
 SO Organometallics (2000), 19(15), 2826-2828
 CODEN: ORGND7; ISSN: 0276-7333
 PB American Chemical Society
 DT Journal
 LA English
 OS CASREACT 133:164142
 AB Treating silicon-bridged ferrocenophane (C₅H₄)₂FeSiMeCl with
 Li[2-C₆H₄CH₂NMe₂] in THF at -78° gave 81% title compound
 (C₅H₄)₂FeSi(2-C₆H₄CH₂NMe₂)Me 2, the structure of which was determined by x-ray
 crystallog. (space group P2₁/n, Z = 4, wR₂ = 0.0827). This
 hypercoordinated Si-bridged [1]ferrocenophane shows a pronounced Si-N
 interaction, a pseudo-trigonal-bipyramidal geometry at the bridging Si
 atom, an elongated Si-Cp bond trans to the amino group, and an unusually
 long Fe-Si distance in comparison to the tetracoordinate analogs.
 Pentacoordination in 2 is suppressed by complexation of the N
 functionality with electrophiles, such as by alkylation
 /quaternization of the N with MeOTf to give an ammonium salt.
 RE.CNT 34 THERE ARE 34 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 4 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
 AN 2000:246808 CAPLUS
 DN 133:17601
 TI Reaction Pathway for the Formation of Binuclear Samarocene Hydride from
 Monomeric Alkyl Samarocene Derivative and the Effective Catalysis of
 Samarocene Hydride for the Block Copolymerization of Ethylene with Polar
 Monomers
 AU Desurmont, Guillaume; Li, Yong; Yasuda, Hajime; Maruo, Tatsuya; Kanehisa,
 Nobuko; Kai, Yasushi
 CS Department of Applied Chemistry Faculty of Engineering, Hiroshima
 University, Higashi-Hiroshima, 739-8527, Japan
 SO Organometallics (2000), 19(10), 1811-1813
 CODEN: ORGND7; ISSN: 0276-7333
 PB American Chemical Society
 DT Journal
 LA English
 OS CASREACT 133:17601
 AB The x-ray anal. of Me₂Si(C₅H₃-3-Me₃Si)₂SmCH(Me₃Si)₂(THF) (1) revealed a
 monomeric structure, while the hydrogenated complex, [Me₂Si(C₅H₃-3-
 Me₃Si)₂SmH(THF)]₂ (2), exhibits binuclear μ-H structure to indicate
 that Me₂SiCp'2M → M(μ-Me₂SiCp'2)₂M rearrangement of the
 η⁵-η⁵ ligation occurs during the hydrogenation. The resulting
 samarocene hydride 2 exhibits high activity as an initiator for the block
 copolymn. of ethylene with polar monomers such as Me methacrylate and
 ε-caprolactone.
 RE.CNT 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 5 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
 AN 1999:760490 CAPLUS
 DN 132:137500
 TI Synthesis and structural characterization of uranium ansa-metallocene
 complexes containing organoimido functional groups; electronic effects of
 ancillary ligands
 AU Schnabel, R. C.; Scott, B. L.; Smith, W. H.; Burns, C. J.
 CS Department of Chemistry, Eckerd College, St. Petersburg, FL, USA
 SO Journal of Organometallic Chemistry (1999), 591(1-2), 14-23
 CODEN: JORCAI; ISSN: 0022-328X
 PB Elsevier Science S.A.
 DT Journal
 LA English
 OS CASREACT 132:137500
 AB Complexes of U(IV) employing the chelating bis(cyclopentadienyl) ligand
 sets [Me₂Si(η⁵-C₅Me₄)₂]₂- and [Me₂Si(η⁵-C₅Me₄)(η⁵-C₅H₄)]₂-
 have been prepared to examine their utility in generating organoimido

complexes of uranium. The chloride complexes $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{UCl}_2 \cdot 2\text{LiCl} \cdot 4(\text{Et}_2\text{O})$ (1) and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)]\text{UCl}_2 \cdot 2\text{LiCl} \cdot 4(\text{THF})$ (2) may be generated at room temperature by reaction of UCl_4 with the corresponding bis(cyclopentadienyl) dilithio salt in di-Et ether and THF, resp. Complex 1 may be recrystd. from toluene in the presence of TMEDA to yield the complex $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{U}(\mu\text{-Cl}_4)\{\text{Li}(\text{TMEDA})\}_2$ (1·TMEDA). The mol. structure of this complex has been determined by single-crystal x-ray diffraction. Compds. 1 and 2 may be alkylated by Grignard reagents. While the di-Me complex $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{UMe}_2$ (3) may be isolated, the analogous complex and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)]\text{UMe}_2$ appears to be thermally unstable. Benzyl derivs. employing both ligand sets $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{U}(\text{CH}_2\text{Ph})_2$ (4) and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)]\text{U}(\text{CH}_2\text{Ph})_2$ (5) have been prepared. These alkyl complexes are protonated by N,N' -diphenylhydrazine to yield phenylimido-containing products. Surprisingly, while reaction of compds. 3 or 4 with N,N' -diphenylhydrazine yields the expected U(VI) complex $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{U}(\text{NC}_6\text{H}_5)_2$, reactions employing 5 generate only the U(IV) monoimido dimer $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)]\text{U}(\text{NC}_6\text{H}_5)_2$ (8). The mol. structure of 8 has been determined; the compound exists as a dimer with asym. organoimido bridging ligands. Electrochem. investigations of the chloride compds. 1 and 2 suggest that the ancillary ligands have the capacity to significantly alter the redox activity of the metal center. The use of electron-rich ancillary ligands appears to be important in the isolation of high-valent organouranium complexes.

RE.CNT 54 THERE ARE 54 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 6 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1999:595699 CAPLUS
DN 131:337127

TI Organometallic compounds of the lanthanides. Part 133. Synthesis and characterization of donor-functionalised ansa-metallocenes of yttrium, neodymium, samarium, erbium, and lutetium
AU Schumann, Herbert; Erbsstein, Frank; Demtschuk, Jorg; Weimann, Roman
CS Institut Anorganische Analytische Chemie, Technische Univ. Berlin, Berlin, D-10623, Germany
SO Zeitschrift fuer Anorganische und Allgemeine Chemie (1999), 625(9), 1457-1465
CODEN: ZAACAB; ISSN: 0044-2313
PB Wiley-VCH Verlag GmbH
DT Journal
LA German
OS CASREACT 131:337127
AB The reaction of Me_2SiCl_2 with $\text{K}[\text{C}_5\text{H}_4\text{tBu}]$, $\text{Li}[\text{C}_5\text{H}_4\text{SiMe}_3]$ or $\text{K}[\text{C}_5\text{H}_3\text{tBu}-3\text{-Me}]$ followed by treatment with $\text{K}[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2]$ yields mixed substituted dicyclopentadienyl(dimethyl)silanes which after double deprotonation with KH afford the dipotassium salts $\text{K}_2[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3-3\text{-tBu})(\text{C}_5\text{H}_3-3\text{-(CH}_2)_2\text{NMe}_2)]$, $\text{K}_2[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3-3\text{-SiMe}_3)(\text{C}_5\text{H}_3-3\text{-(CH}_2)_2\text{NMe}_2)]$, and $\text{K}_2[\text{Me}_2\text{Si}(\text{C}_5\text{H}_2-3,5\text{-tBuMe})(\text{C}_5\text{H}_3-3\text{-(CH}_2)_2\text{NMe}_2)]$, resp. Subsequent reaction with $\text{LnCl}_3(\text{THF})_x$ ($\text{Ln} = \text{Y, La, Nd, Sm, Er, Lu}$) leads to $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3-3\text{-tBu})(\text{C}_5\text{H}_3-3\text{-(CH}_2)_2\text{NMe}_2)]\text{LnCl}$ (I; $\text{Ln} = \text{Y, Sm, Lu}$), $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3-3\text{-SiMe}_3)(\text{C}_5\text{H}_3-3\text{-(CH}_2)_2\text{NMe}_2)]\text{LnCl}$ (II; $\text{Ln} = \text{Y, Sm, Lu}$), and $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_2-3,5\text{-tBuMe})(\text{C}_5\text{H}_3-3\text{-(CH}_2)_2\text{NMe}_2)]\text{LnCl}$ (III; $\text{Ln} = \text{Y, Nd, Sm, Er, Lu}$), resp. Alkylation of I ($\text{Ln} = \text{Y, Sm}$), II ($\text{Ln} = \text{Y}$), and III ($\text{Ln} = \text{Nd, Lu}$) with LiMe , $\text{LiCH}_2\text{SiMe}_3$, and $\text{LiCH}(\text{SiMe}_3)_2$ produces the alkylmetallocenes $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3-3\text{-tBu})(\text{C}_5\text{H}_3-3\text{-(CH}_2)_2\text{NMe}_2)]\text{LnR}$ ($\text{R} = \text{Me, Ln} = \text{Y, Sm}$, $\text{R} = \text{CH}_2\text{SiMe}_3$, $\text{Ln} = \text{Y}$), $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3-3\text{-SiMe}_3)(\text{C}_5\text{H}_3-3\text{-(CH}_2)_2\text{NMe}_2)]\text{YMe}$, and $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_2-3,5\text{-tBuMe})(\text{C}_5\text{H}_3-3\text{-(CH}_2)_2\text{NMe}_2)]\text{LnR}$ ($\text{R} = \text{Me, Ln} = \text{Lu}$; $\text{R} = \text{CH}_2\text{SiMe}_3$, $\text{Ln} = \text{Lu}$; $\text{R} = \text{CH}(\text{SiMe}_3)_2$, $\text{Ln} = \text{Nd, Lu}$), resp. All new compds. were characterized by elemental anal., NMR, and mass spectrometry. The mol. structure of III ($\text{Ln} = \text{Sm, Lu}$) was determined by single crystal x-ray structure anal.

RE.CNT 45 THERE ARE 45 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 7 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1999:505693 CAPLUS
DN 131:116377
TI Metallocene synthesis

IN Lin, Ronny W.; Berris, Bruce C.; Power, John M.; DeSoto, Troy E.; Balhoff,
John F.; Strickler, Jamie R.
PA Albemarle Corporation, USA
SO U.S., 9 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5936108	A	19990810	US 1997-998105	19971224 <--
PRAI	US 1996-730801	B2	19961017		

OS MARPAT 131:116377

AB A metallocene having one or two hydrocarbyl groups bonded to a Group 4 metal are produced from a crude impure pasty or non-wet mixture containing at least 50% by weight of a metallocene having two halogen atoms bonded to a Group 4 metal atom, by (a) mixing liquid aromatic hydrocarbon with the crude impure pasty or non-wet mixture; (b) mixing a solution of an organolithium compound in a suitable anhydrous ether or paraffinic hydrocarbon solvent or a mixture thereof, with the mixture from (a) and agitating the resulting mixture so that lithium halide solids are formed; and (c) separating the solids and recovering the resultant liquid portion which is mainly a solution of the metallocene having one or two hydrocarbyl groups bonded to a Group 4 metal. Addnl. optional steps include (d) replacing the original solvent from the solution from (c) with a liquid paraffinic hydrocarbon diluent to form a slurry of product solids; and (e) recovering the product metallocene solids. Preferred organolithium compds. have the formula, $RLi.nLiX$, where R is tert-alkyl, aryl, alkaryl, benzyl, or alkyl-substituted benzyl, or most preferably, Me, and X is Br or I. Thus, rac-dimethylsilylbisindenylhafnium dichloride (4.93 82 weight % purity; 7.54 mmol) was placed in a 200 mL Shlenk flask with 56.7 g of toluene. Most of the orange yellow metallocene remained undissolved. The slurry was heated to 34° and a solution of $MeLi.nLiBr$ (1.5M in Et_2O) was added dropwise over two hours. The solution became yellow-orange and the solids lightened to a beige color. The reaction was allowed to cool to ambient temperature and stir overnight to give 83% rac-dimethylsilylbisindenylhafnium di-Me.

RE.CNT 37 THERE ARE 37 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 8 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1998:724715 CAPLUS
DN 130:66569

TI New ansa-Niobocene Complexes. X-ray Crystal Structure of
[$Me_2Si(\eta^5-C_5H_4)_2$]Nb(:NtBu)Cl. Stereoselective Synthesis of
meso-[$Me_2Si(\eta^5-C_5H_3SiMe_3)_2$]Nb(:NtBu)Cl

AU Antinolo, Antonio; Otero, Antonio; Prashar, Sanjiv; Rodriguez, Ana M.
CS Departamento de Quimica Inorganica Organica y Bioquimica Facultad de
Quimicas Campus Universitario, Universidad de Castilla-La Mancha, Ciudad
Real, 13071, Spain

SO Organometallics (1998), 17(25), 5454-5459
CODEN: ORGND7; ISSN: 0276-7333

PB American Chemical Society

DT Journal

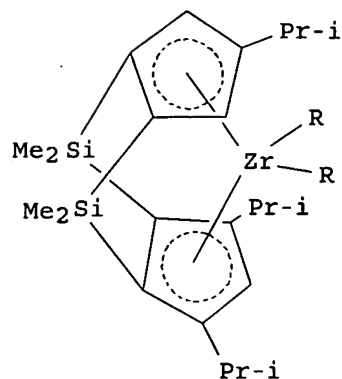
LA English

OS CASREACT 130:66569

AB The ansa-niobocene complex [$Me_2Si(\eta^5-C_5H_4)_2$]Nb(:NtBu)Cl (1) was prepared and its structure determined by single-crystal x-ray diffraction. The alkyl complexes [$Me_2Si(\eta^5-C_5H_4)_2$]Nb(:NtBu)(R) (R = Me (2), Et (3), CH_2Ph (4), $CH_2CH:CH_2$ (5)) were prepared by the reaction of 1 and the corresponding Grignard reagent. Using the trimethylsilyl-substituted ansa ligand $Me_2Si(C_5H_3SiMe_3)_2$, [$Me_2Si(\eta^5-C_5H_3SiMe_3)_2$]Nb(:NtBu)Cl (6) was prepared and isolated uniquely as the meso-isomer. Nevertheless the synthesis of [$Me_2Si(\eta^5-C_5H_3SiMe_3)_2$]NbCl₂ (7) yielded a mixture of meso- and rac-isomers. Reduction of 7 in the presence of ligand (RC.tplbond.CR) (R = Me, Ph) gave [$Me_2Si(\eta^5-C_5H_3SiMe_3)_2$]NbCl(RC.tplbond.CR) (R = Me (8), Ph (9)). Both complexes were initially isolated as mixts. of meso- and rac-isomers and in the case of 9 could be separated due to their differing solubilities in hexane.

RE.CNT 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD

L6 ANSWER 9 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
 AN 1998:639473 CAPLUS
 DN 130:3914
 TI Preparation of doubly-silylene-bridged zirconocene alkyl complexes,
 $(\text{Me}_2\text{Si})_2\{\eta^5\text{-C}_5\text{H}_2\text{-4-CHMe}_2\}\{\eta^5\text{-C}_5\text{H-3,5-(CHMe}_2)_2\}\text{ZrR}_2$ ($\text{R} = \text{CH}_3$,
 CH_2Ph) and investigations of their activity in 1-pentene polymerization.
 Molecular structure of $(\text{Me}_2\text{Si})_2\{\eta^5\text{-C}_5\text{H}_2\text{-4-CHMe}_2\}\{\eta^5\text{-C}_5\text{H-3,5-}$
 $(\text{CHMe}_2)_2\}\text{Zr}(\text{CH}_2\text{Ph})_2$
 AU Veghini, Dario; Day, Michael W.; Bercaw, John E.
 CS Arnold and Mabel Beckman Lab. Chem. Synthesis, California Inst. Technol.,
 Pasadena, 91125, USA
 SO Inorganica Chimica Acta (1998), 280(1-2), 226-232
 CODEN: ICHAA3; ISSN: 0020-1693
 PB Elsevier Science S.A.
 DT Journal
 LA English
 GI



AB The syntheses of the doubly-silylene-bridged zirconocene complexes, I [$\text{R} =$
 Cl (2); CH_2Ph (3); CH_3 (4)] are described. 2 Reacted with $\text{K}[\text{CH}_2\text{Ph}]/\text{Et}_2\text{O}$
 and $\text{LiMe}/\text{Et}_2\text{O}$ to give 3 and 4, resp. The structure of 3 was examined by
 single crystal x-ray diffraction methods. It crystallizes in the
 triclinic space group P-1, with a 9.900(2), b 11.818(2), c 15.320(3) Å,
 α 105.02(3), β 92.56(3), γ 105.23(3)° and Z = 2.
 Compds. 3 and 4 are active stereospecific pre-catalysts for the
 $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ co-catalyzed polymerization of 1-pentene. Polymerization reactions at
 low temperature in liquid monomer produced poly(1-pentene) with syndiotactic
 microstructure and narrow mol. weight distribution. By contrast, in
 1-pentene/toluene solns. a broad mol. weight distribution is observed. Under all
 conditions examined 2/MAO systems produced high mol. weight, highly
 syndiotactic poly-1-pentene with narrow mol. weight distributions.
 RE.CNT 47 THERE ARE 47 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 10 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
 AN 1998:527109 CAPLUS
 DN 129:176102
 TI Preparation of a metallocene catalyst system
 IN Fritze, Cornelia; Bohnen, Hans; Kuber, Frank
 PA Hoechst A.-G., Germany; Basell Polyolefine GmbH
 SO Eur. Pat. Appl., 21 pp.
 CODEN: EPXXDW
 DT Patent
 LA German
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 856523	A1	19980805	EP 1998-100330	19980110 <--
	EP 856523	B1	20040714		
	R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI				
	DE 19703478	A1	19980806	DE 1997-19703478	19970131 <--
	AT 271070	E	20040715	AT 1998-100330	19980110
	US 6177376	B1	20010123	US 1998-15130	19980129 <--
	JP 10218921	A2	19980818	JP 1998-18456	19980130 <--
	BR 9800515	A	19990706	BR 1998-515	19980130 <--
PRAI	DE 1997-19703478	A	19970131		

OS MARPAT 129:176102

AB A metallocene is treated with a compound bearing a hydrocarbyl group in a solvent to form a hydrocarbyl group-substituted (via a σ bond) metallocene, which is used in solution, without isolation or purification, with an activator as a polymerization catalyst. Thus, [(dimethylsilylene)bis(2-methyl-4-phenylindenyl)]zirconium dichloride was treated with MeMgBr in toluene to form [(dimethylsilylene)bis(2-methyl-4-phenylindenyl)]dimethylzirconium (I), which was activated by addition of PhN+HMe2 -B(C6F5)4. A similar I-containing catalyst deposited on SiO2 was used to polymerize propylene at 60°, yielding 126 kg polypropylene/g metallocene per h.

RE.CNT 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 11 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1997:588388 CAPLUS

DN 127:262786

TI Enantiomerically Pure Organolanthanides for Asymmetric Catalysis.
Synthesis, Structures, and Catalytic Properties of Complexes Having
Pseudo-meso-Me2Si(η 5-C5H3R)(η 5-C5H3R*) Ancillary Ligation

AU Roesky, Peter W.; Denninger, Uwe; Stern, Charlotte L.; Marks, Tobin J.
CS Department of Chemistry, Northwestern University, Evanston, IL,
60208-3113, USA

SO Organometallics (1997), 16(20), 4486-4492

CODEN: ORGND7; ISSN: 0276-7333

PB American Chemical Society

DT Journal

LA English

OS CASREACT 127:262786

AB As established by NMR, CD, and x-ray diffraction, organolanthanides of the new chelating ligand Me2Si(tBuCp)[(+)-neo-Men-Cp]2- (Cp = η 5-C5H3) preferentially adopt a single chiral configuration of the asym. metal-ligand template. Metallocene dichloro complexes (R,S)-Me2Si(tBuCp)[(+)-neo-Men-Cp]Ln(μ -Cl)2Li(OEt2)2 (Ln = Y, Lu) were synthesized by alkylation of the corresponding lanthanide trichlorides with the ligand dilithium salt and were isolated isomerically pure by crystallization from Et2O. Alkylation of the (R,S)-epimers with MCH(SiMe3)2 (M = Li, K) proceeds with retention of configuration at the lanthanide center, affording chiral hydrocarbyl complexes in high yield. Reaction of the Lu-hydrocarbyl with H2 affords diastereomerically pure {(R,S)-Me2Si(tBuCp)[(+)-neo-Men-Cp]LuH}2, an active catalyst for asym. olefin hydrogenation. X-ray diffraction reveals a pseudo-C2-sym. dimer with a pseudo-meso Cp ring substituent arrangement. The two Me2Si(tBuCp)[(+)-neo-Men-Cp]LuH fragments are slightly twisted with respect to each other. These hydrocarbyls are effective precatalysts for asym. hydrogenation of unfunctionalized olefins. The ee values obtained for deuteration of 1-pentene (up to 63%) are the highest reported to date for this reaction, and in all reactions, the (R)-product enantiomer is favored. These results together with those obtained using other chiral organolanthanides provide better insight into lanthanocene stereochem. preferences and chirality transfer mechanisms.

RE.CNT 61 THERE ARE 61 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 12 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1997:377776 CAPLUS

DN 127:66245

TI Ancillary Ligand Effects in Chiral C1-Symmetric ansa-Metallocene Catalysts

for Stereoregular α -Olefin Polymerization. "Wingspan" Modification with Octahydrofluorene

AU Obora, Yasushi; Stern, Charlotte L.; Marks, Tobin J.; Nickias, Peter N.
CS Department of Chemistry, Northwestern University, Evanston, IL,
60208-3113, USA

SO Organometallics (1997), 16(12), 2503-2505
CODEN: ORGND7; ISSN: 0276-7333

PB American Chemical Society

DT Journal

LA English

AB The synthesis and activity as precatalysts for stereoregular α -olefin polymerization of the chiral Cl-sym. zirconocene complexes (R)- and (S)-Me₂Si(η 5-C₁₃H₁₆)(η 5-C₅H₃R*)ZrR₂ where C₁₃H₁₆-octahydrofluorenyl, R: NMe₂, Cl, or Me, and R* = (1R,2S,5R)-trans-5-methyl-cis-2-(2-propyl)cyclohexyl((-)-menthyl) are described. The highly (S)-enriched (\geq 90%) zirconocene dichloride complex is prepared from the corresponding bis(dimethylamide) complex with Me₂NH.HCl and converted to the corresponding di-Me complex by MeLi alkylation. These complexes were characterized by techniques with absolute configuration established by chiral dichroism and X-ray diffraction. Propylene polymerization catalysts were generated via the reaction of the dichloride complex with MAO or the reaction of the di-Me complex with B(C₆F₅)₃ or Ph₃C+B(C₆F₅)₄-. The resulting catalysts effect substantially greater isoselection than either the η 5-tetramethylcyclopentadienyl or η 5-fluorenyl analogs.

RE.CNT 46 THERE ARE 46 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 13 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1997:207599 CAPLUS

DN 127:65875

TI β -Hydrogen-Containing Zirconium Alkyls with the Doubly-Bridged Bis(dimethylsilanediyl)dicyclopentadienyl Ligand. X-ray Molecular Structures of [Zr{(SiMe₂)₂(η 5-C₅H₃)₂}ClEt] and [Zr{(SiMe₂)₂(η 5-C₅H₃)₂}Et]₂(μ -CH₂:CH₂)

AU Fernandez, Francisco J.; Gomez-Sal, Pilar; Manzanero, Antonio; Royo, Pascual; Jacobsen, Heiko; Berke, Heinz

CS Departamento de Quimica Inorganica Facultad de Ciencias, Universidad de Alcala de Henares, Alcala de Henares, 28871, Spain

SO Organometallics (1997), 16(8), 1553-1561
CODEN: ORGND7; ISSN: 0276-7333

PB American Chemical Society

DT Journal

LA English

OS CASREACT 127:65875

AB Alkylation of [Zr(CpSi₂Cp)Cl₂] [CpSi₂Cp = (η 5-C₅H₃)₂(SiMe₂)₂] with 1 equiv of RMgCl in THF at 10° gave the monoalkylated complexes [Zr(CpSi₂Cp)ClR] (R = Et, Pr, i-Pr) in 80% yield, the iso-Pr complex isomerizing to the Pr derivative >10°. Addition of a 2nd equivalent or an excess amount of the alkylating agent gave the dialkyl compds. [Zr(CpSi₂Cp)R₂] (R = Et, Pr). Hydrolysis of [Zr(CpSi₂Cp)ClR] led to the μ -oxo dinuclear complex [{Zr(CpSi₂Cp)Cl}₂(μ -O)]. Thermal decomposition of THF solns. of [Zr(CpSi₂Cp)ClR] takes place with the evolution of an equimolar amount of alkane and alkene and the formation of [Zr(CpSi₂Cp)Cl₂] and an unidentified residue. Formation of [Zr(CpSi₂Cp)Et₂] is always accompanied by decomposition with the evolution of ethane to give [{Zr(CpSi₂Cp)Et}₂(μ -CH₂:CH₂)] in 70% yield. A similar behavior was observed for [Zr(CpSi₂Cp)Pr₂]. All of the compds. were characterized by elemental anal. and NMR spectroscopy, and the mol. structures of [Zr(CpSi₂Cp)ClEt] and [{Zr(CpSi₂Cp)Et}₂(μ -CH₂:CH₂)] were studied by x-ray diffraction methods: D. functional calcns. on the model compound [{ZrCp₂Me}₂(μ -CH₂:CH₂)] satisfactorily reproduce the geometry found exptl. (dC-C = 1.482, d₁Zr-C = 2.327 Å, d₂Zr-C = 2.506 Å).

RE.CNT 50 THERE ARE 50 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 14 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1996:156889 CAPLUS

DN 124:289742

TI Coordinative Unsaturation in Chiral Organolanthanides. Synthetic and

Asymmetric Catalytic Mechanistic Study of Organoyttrium and -lutetium
Complexes Having Pseudo-Meso Me₂Si(η⁵-RC₅H₃)(η⁵-RC₅H₃) Ancillary
Ligation

AU Haar, Christopher M.; Stern, Charlotte L.; Marks, Tobin J.
CS Department of Chemistry, Northwestern University, Evanston, IL,
60208-3113, USA
SO Organometallics (1996), 15(7), 1765-84
CODEN: ORGND7; ISSN: 0276-7333
PB American Chemical Society
DT Journal
LA English
OS CASREACT 124:289742
AB As established by NMR, CD, and x-ray diffraction, organolanthanide
complexes of the new chelating ligand Me₂Si(3-Me₃SiCp)[3-(-)-menthylCp]₂-
(Cp = η⁵-C₅H₃) preferentially adopt a single planar chiral
configuration of the asym. metal-ligand template. Chloro complexes
(S,R)-Me₂Si(Me₃SiCp)[(-)-menthylCp]Ln(μ-Cl)₂Li(OEt)₂ (Ln = Y, Lu) were
isolated diastereomerically pure by crystallization from di-Et ether. The unusual
pseudo-meso configuration leads to a gross distortion from ideal C_{2v}
symmetry, evidenced by a significant deviation of ∠Sibridge-Lu-Li
from linearity (158°). At least two addnl. epimers are detected in
THF solution. Alkylation of the (S,R) epimers with LiCH(SiMe₃)₂
proceeds with retention of configuration, affording chiral hydrocarbyl
complexes in quant. yield. In solution, the hydrocarbyls exhibit
temperature-dependent conformational exchange processes in the NMR ascribable to
restricted rotation about the Ln-CH(SiMe₃)₂ bond. These complexes are
effective precatalysts for asym. hydrogenation of unfunctionalized olefins
and for the reductive cyclization of 1,5-dienes. The highest
enantioselectivities are obtained when the Lu complex is used for
hydrogenation of 2-phenyl-1-butene (45% ee) and deuteration of styrene
(10% ee) and 1-pentene (30% ee). The hydrogenation of 2-phenyl-1-butene
with the Y catalyst (yielding exclusively 2-phenylbutane-1,2-d₂ under D₂)
obeys a rate law of the approx. form v = (k[olefin]¹[lanthanide]^{1/2}[H₂]¹)/
(K + [olefin]), suggesting rapid, operationally irreversible olefin
insertion at a putative hydride, a rapid preequil. involving an alkyl or
alkyl/hydride dimer, and turnover-limiting hydrogenolysis of an
intermediate yttrium alkyl with vH₂/vD₂ = 2.2 ± 0.1. The apparent rate
constant for 2-phenyl-1-butene hydrogenation (12(1) + 10⁻³ M^{1/2} atm⁻¹
s⁻¹) is ca. 1 order of magnitude lower than for chiral
Me₂Si(Me₄C₅)(3-R^{*}Cp)Ln-based systems (R^{*} = (-)-menthyl, (+)-neomenthyl; Ln
= Y, La, Nd, Sm, Lu), principally reflecting diminished Ln-C bond
hydrogenolytic reactivity.

L6 ANSWER 15 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1995:758697 CAPLUS
DN 123:144279
TI Preparation of racemic metallocene complexes as catalysts for olefin
polymerization
IN Langhauser, Franz Dr; Kerth, Juergen Dr; Schweier, Guenther Dr;
Brintzinger, Hans-Herbert; Mansel, Stefan
PA BASF A.-G., Germany
SO Eur. Pat. Appl., 16 pp.
CODEN: EPXXDW
DT Patent
LA German
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 650973	A1	19950503	EP 1994-116511	19941020 <--
	EP 650973	B1	19990310		
	R: BE, DE, ES, FR, GB, IT, NL				
	DE 4337232	A1	19950504	DE 1993-4337232	19931030 <--
	ES 2128486	T3	19990516	ES 1994-116511	19941020 <--
	US 5554776	A	19960910	US 1994-328777	19941028 <--
	US 5670683	A	19970923	US 1996-620318	19960322 <--
PRAI	DE 1993-4337232	A	19931030		
	US 1994-328777	A3	19941028		
OS	CASREACT 123:144279; MARPAT 123:144279				
GI					

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The preparation of title compds. I (M = Ti, Zr, Hf, V, Nb, Ta; X = F, Cl, Br, iodo, H, C1-10 alkyl, C6-15 aryl, alkoxy, etc.; R1-R6 = C1-10 alkyl, C5-7 cycloalkyl, C1-10 substituted alkyl, C6-15 aryl or arylalkyl, etc.; Y1, Y2 = Si, Ge, or Sn containing hydrocarbyl, alkylenyl, etc.), useful as catalysts for olefin polymerization, is described. Thus, lithiation of spiroasilane II (preparation given) with BuLi in pentane/hexane followed by treatment with ZrCl₄ gave title compound III.

L6 ANSWER 16 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1995:494394 CAPLUS
DN 122:240692
TI Homogeneous catalysts for stereoregular olefin polymerization
IN Marks, Tobin J.; Eisen, Moris S.; Giardello, Michael A.
PA Northwestern University, USA
SO U.S., 7 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5330948	A	19940719	US 1992-860784	19920331 <--
	US 5312881	A	19940517	US 1993-25372	19930226 <--
	US 5455317	A	19951003	US 1995-373869	19950117 <--
PRAI	US 1992-860784	A2	19920331		
	US 1994-191989	B1	19940204		

OS MARPAT 122:240692
AB Precatalyst complexes for olefin polymerization have the structure (C₅R'⁴-xR*x) A (C₅R''⁴-yR''^y) M Q_p, where x and y represent the number of unsubstituted locations on the cyclopentadienyl ring; R', R'', R''', and R* represent substituted and unsubstituted alkyl groups having 1-30 carbon atoms and R* is a chiral ligand; A is a fragment containing a Group 13, 14, 15, or 16 element of the Periodic Table; M is a Group 3, 4, or 5 metal of the Periodic Table; and Q is a hydrocarbyl radical, or halogen radical, with 3 ≤ p ≤ ∞. Related complexes may be prepared by alkylation of the corresponding dichlorides. In the presence of methylalumoxane or triarylborane cocatalysts, these complexes form "cation-like" species which are highly active for olefin polymerization. In combination with a Lewis acid cocatalyst, propylene or other α-olefin polymerization can be effected with very high efficiency and isospecificity.

L6 ANSWER 17 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1995:130601 CAPLUS
DN 122:56143
TI Chiral Organolanthanides Designed for Asymmetric Catalysis. Synthesis, Characterization, and Configurational Interconversions of Chiral, C1-Symmetric Organolanthanide Halides, Amides, and Hydrocarbyls
AU Giardello, Michael A.; Conticello, Vincent P.; Brard, Laurent; Sabat, Michal; Rheingold, Arnold L.; Stern, Charlotte L.; Marks, Tobin J.
CS Department of Chemistry, Northwestern University, Evanston, IL, 60208-3113, USA
SO Journal of the American Chemical Society (1994), 116(22), 10212-40
CODEN: JACSAT; ISSN: 0002-7863

DT Journal
LA English
AB This contribution describes the synthesis, structural systematics, absolute configurations, and structural interconversions of a series of C1-sym. lanthanide chloro, hydrocarbyl, and amide complexes/precatalysts based on chiral chelating Me₂Si(η⁵-Me₄C₅)(η⁵-C₅H₃R*)₂- ligands [Me₂SiCp''(R*Cp)]₂-, where R* = (+)-neomenthyl, (-)-menthyl, and (-)-phenylmenthyl. The ligands are prepared in three steps from known

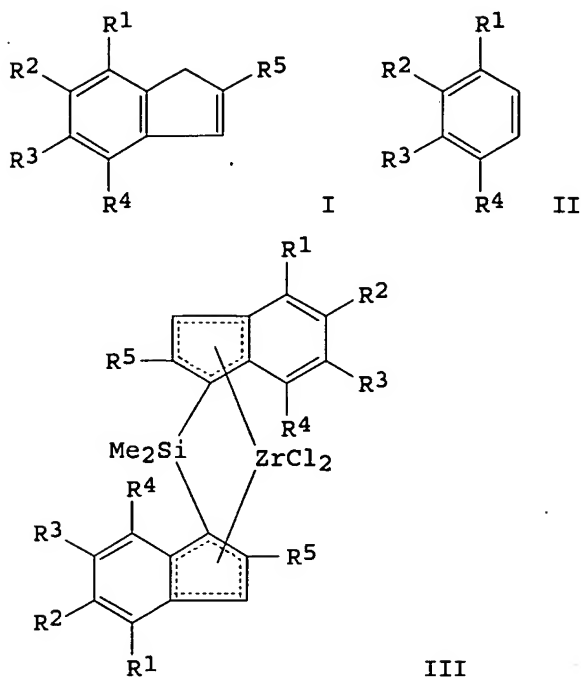
chiral cyclopentadienes. Metalation of the chiral dienes followed by condensation with Me₄C₅SiMe₂Cl and in situ lithiation provides the dianions in nearly quant. yield. Transmetalation of the lithiated ligands with anhydrous lanthanide trichlorides followed by ambient temperature ether workup provides Me₂SiCp''(R*Cp)LnCl₂Li(OEt)₂ complexes in high yield. For the crystal structure of (R)-Me₂SiCp''[(+)-neomenthylCp]Lu(μ-Cl)₂Li(OEt)₂ was determined As established by NMR and CD, the diastereomerically pure chloro complexes can be epimerized in appropriate donor solvents to afford mixts. of (R)- and (S)-configurational isomers with the isomer ratio dependent on solvent, R*, and lanthanide ion. Selective epimerization allows enrichment in either antipode with diastereomerically pure complexes obtained in a single recrystn. Li⁺ sequestering crown ethers inhibit epimerization. The temperature dependence of the (R) .dblharw. (S) equilibrium constant in THF yields ΔH = 1.7 ± 0.3 kcal/mol and ΔS = 3.6 ± 0.8 eu for Me₂SiCp''[(+)-neomenthylCp]Lu(μ-Cl)₂Li(OEt)₂ and ΔH = 4.8 ± 0.5 kcal/mol and ΔS = 13.4 ± 0.5 eu for Me₂SiCp''[(-)-menthylCp]Sm(μ-Cl)₂Li(OEt)₂. The mechanism is proposed to involve reversible ring detachment to an intermediate LiCpR* complex. Alkylation or amidation with ME(SiMe₃)₂ (M = Li or K, E = CH; M = Na or K, E = N) yields the corresponding chiral hydrocarbyls and amides in high yield. The crystal structures of (R/S)-Me₂SiCp''[(+)-neomenthylCp]YCH(SiMe₃)₂, (R)-Me₂SiCp''[(-)-menthylCp]SmCH(SiMe₃)₂, (R)-Me₂SiCp''[(-)-menthylCp]YCH(SiMe₃)₂, (S)-Me₂SiCp''[(+)-neomenthylCp]SmN(SiMe₃)₂, (S)-Me₂SiCp''[(-)-menthylCp]SmN(SiMe₃)₂ and (R)-Me₂SiCp''[(-)-menthylCp]YN(SiMe₃)₂ were determined The preferred planar chiral configurations of these complexes can be largely understood from significant,crystallog. identifiable, nonbonded interactions between R* and the remainder of the mol. The hydrocarbyl and amide complexes are configurationally stable in toluene at 60° for many hours but undergo facile epimerization in the presence of primary alkyl amines, presumably via reversible Cp protonation/detachment. The hydrocarbyl complexes undergo rapid hydrolysis at ambient temperature, with retention of configuration, to yield the corresponding hydrides.

L6 ANSWER 18 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
 AN 1993:650177 CAPLUS
 DN 119:250177
 TI Process for the preparation of substituted indenenes and their use as
 ligands for metallocene olefin polymerization catalysts
 IN Rohrmann, Juergen; Kueber, Frank
 PA Hoechst A.-G., Germany
 SO Eur. Pat. Appl., 20 pp.
 CODEN: EPXXDW
 DT Patent
 LA German
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 545304	A1	19930609	EP 1992-120289	19921127 <--
	EP 545304	B1	20020619		
	R: AT, BE, CH, DE, ES, FR, GB, IT, LI, LU, NL, SE				
	ZA 9209215	A	19930527	ZA 1992-9215	19921127 <--
	CA 2084016	AA	19930531	CA 1992-2084016	19921127 <--
	CA 2084016	C	20040622		
	AU 9229727	A1	19930603	AU 1992-29727	19921127 <--
	AU 655088	B2	19941201		
	JP 06206890	A2	19940726	JP 1992-319101	19921127 <--
	JP 3290218	B2	20020610		
	AT 219494	E	20020715	AT 1992-120289	19921127
	JP 2002226405	A2	20020814	JP 2001-379159	19921127
	JP 3434288	B2	20030804		
	ES 2177523	T3	20021216	ES 1992-120289	19921127
	RU 2103250	C1	19980127	RU 1992-4483	19921130 <--
	US 5840948	A	19981124	US 1995-462587	19950605 <--
	US 5852142	A	19981222	US 1995-462588	19950605 <--
	US 6051522	A	20000418	US 1995-464459	19950605 <--
	US 5929264	A	19990727	US 1997-890942	19970710 <--
PRAI	DE 1991-4139594	A	19911130		
	US 1992-980993	B1	19921124		

JP 1992-319101 A3 19921127
 US 1994-291738 B3 19940817
 US 1995-462587 A1 19950605
 CASREACT 119:250177; MARPAT 119:250177

OS
 GI



AB A process for the preparation of indene derivs. of formula I wherein R1-R5 are the same or different and may be H, alkyl, aryl, alkoxy, haloaryl, etc., comprises treatment of aryl compds. II with R5CMe(X1)C(O)X2 [X1, X2 = halo; e.g., X = Br, R5 = H] in the presence of a Friedel-Crafts catalyst, e.g., AlCl3, to give the corresponding indanone, followed by a reductive elimination with NaBH4. Silylation of I by sequential treatment with BuLi and diorganodichlorosilanes gave a bis(indenyl)silane intermediate which upon treatment with ZrCl4 gave silanediylmetallocene complexes such as III. III were examined for catalytic activity in the polymerization of propylene.

L6 ANSWER 19 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1992:531601 CAPLUS

DN 117:131601

TI Iso-specific Ziegler-Natta polymerization of α -olefins with a single-component organoyttrium catalyst

AU Coughlin, E. Bryan; Bercaw, John E.

CS Arnold and Mabel Beckman Lab. Chem. Synth., California Inst. Technol., Pasadena, CA, 91125, USA

SO Journal of the American Chemical Society (1992), 114(19), 7606-7
 CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

AB The synthesis of Me2Si(2-SiMe3-4-CMe3-C5H2)2Y(μ -Cl)2Li(THF)2 (I) by reaction of Li2[Me2Si(2-SiMe3-4-CMe3-C5H2)2] with YCl3(THF)3 yields exclusively the racemo C2 sym. product. Alkylation of I with LiCH(SiMe3)2 followed by hydrogenolysis yields [rac-Me2Si(2-SiMe3-4-CMe3-C5H2)2YH]2(II). Propylene (25 volume% in methylcyclohexene) and neat samples of 1-butene, 1-pentene, and 1-hexene are polymerized by II to produce highly isotactic polymers. 13C-NMR spectra at the pentad anal. level indicates that the degree of isotacticity is >99% for all polymer samples.

L6 ANSWER 20 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1992:174325 CAPLUS

DN 116:174325
 TI Chiral organolanthanide complexes for enantioselective olefin hydrogenation
 AU Conticello, Vincent P.; Brard, Laurent; Giardello, Michael A.; Tsuji, Yasushi; Sabat, Michal; Stern, Charlotte L.; Marks, Tobin J.
 CS Dep. Chem., Northwestern Univ., Evanston, IL, 60208-3113, USA
 SO Journal of the American Chemical Society (1992), 114(7), 2761-2
 CODEN: JACSAT; ISSN: 0002-7863
 DT Journal
 LA English
 OS CASREACT 116:174325
 AB The synthesis and activity as precatalysts for enantioselective olefin hydrogenation of four chiral organolanthanide complexes, (R)- and (S)-Me₂Si(Me₄C₅)(C₅H₃R*)SmCH(SiMe₃)₂ [R* = (1S,2S,5R)-trans-5-methyl-cis-2-(2-propyl)cyclohexyl [(+)-neomenthyl] and (1R,2S,5R)-cis-5-methyl-trans-2-(2-propyl)cyclohexyl [(-)-menthyl]] are reported. These hydrocarbyls were prepared by alkylation of the corresponding Me₂Si(Me₄C₅)(C₅H₃R*)SmCl₂Li(OEt)₂ complexes and were characterized by standard techniques, including CD and x-ray diffraction. For the (S)-R* = (+)-neomenthyl complex, diffraction-quality crystals could only be obtained for a 1:1 (R):(S) mixed crystal. An yttrium analog was also prepared and characterized by x-ray crystallog. These complexes catalyze the reduction of 2-phenyl-1-butene and styrene with turnover-frequencies as high as 20,000 h⁻¹ (25°, PH₂ = 1 atm) and % enantiomeric excesses as high as 80% (25°) and 96% (-78°). Pseudoenantiomorphous complexes yield products of opposite configuration. The rate law for 2-phenyl-1-butene hydrogenation is: $v = k[\text{Sm}]^{1/2}[\text{H}_2]^{1/2}[\text{olefin}]^0$.

L6 ANSWER 21 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
 AN 1991:449866 CAPLUS
 DN 115:49866
 TI Dialkyl- and chloroalkyltitanium ansa-metallocene complexes: synthesis and characterization. Crystal structure of [η⁵-η⁵-(C₅H₄)₂Si(CH₃)₂]TiClCH₃
 AU Gomez, Rafael; Cuenca, Tomas; Royo, Pascual; Hovestreydt, Eric
 CS Dep. Quim. Inorg., Univ. Alcala de Henares, Alcala de Henares, 28871, Spain
 SO Organometallics (1991), 10(7), 2516-18
 CODEN: ORGND7; ISSN: 0276-7333
 DT Journal
 LA English
 OS CASREACT 115:49866
 AB Dialkyl and chloroalkyl ansa-titanocene complexes [η⁵-η⁵-(C₅H₄)₂SiMe₂]TiR₂ [R = Me, Bz, o-xylidene] and [η⁵-η⁵-(C₅H₄)₂Si(CH₃)₂]TiClR [R = Me, CH₂SiMe₃, SiMe₃] were prepared by reacting the ansa-metallocene dihalide [η⁵-η⁵-(C₅H₄)₂SiMe₂]TiCl₂ with the adequate alkyl reagent.

L6 ANSWER 22 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
 AN 1991:229076 CAPLUS
 DN 114:229076
 TI Group 4 ansa-metallocenes in oxidation state (III): synthesis, characterization, and chemical behavior. Crystal structure of [[η⁵:η⁵-(C₅H₄)₂Si(CH₃)₂]TiCl(PMe₂Ph)]
 AU Gomez, Rafael; Cuenca, Tomas; Royo, Pascual; Pellinghelli, Maria Angela; Tiripicchio, Antonio
 CS Dep. Quim. Inorg., Univ. Alcala de Henares, Alcala de Henares, E-28871, Spain
 SO Organometallics (1991), 10(5), 1505-10
 CODEN: ORGND7; ISSN: 0276-7333
 DT Journal
 LA English
 OS CASREACT 114:229076
 AB Two new dimeric titanium(III) and zirconium(III) ansa-metallocenes [[(Me₂SiCp₂)MCl]₂] [M = Ti(III), Zr] were synthesized by reducing the dichlorometallocenes with Na/Hg. The same reduction of the titanium derivative in the presence of PMe₂Ph led to the monomeric titanium(III) complex [(Me₂SiCp₂)TiCl(PMe₂Ph)] (II), which was also obtained by addition of PMe₂Ph to I. Alkylation of (II) led to the titanium(III) alkyls

[(Me₂SiCp₂)TiR(PMe₂Ph)] (R = Me, CH₂SiMe₃) which was also obtained by reduction of [(Me₂SiCp₂)TiClMe] with Na/Hg in the presence of PMe₂Ph. All the titanium(III) complexes were paramagnetic, and their EPR behavior was studied, whereas the diamagnetic zirconium(III) derivs. were characterized by NMR spectroscopy. All of them are easily oxidized by oxygen, and the intermediate dimeric [(μ-O)[(Me₂SiCp₂)ZrCl]₂] was spectroscopically identified in solution. The structure of (II) was determined by x-ray diffraction methods. The structure of (II) is very similar to that of comparable Ti(IV) compound [(Me₂SiCp₂)TiCl₂], except for the much longer Ti-Cl bond (2.463 (2) against 2.356 (1) and 2.379 (2) Å), whereas no significant modifications are induced into the dimethylsilyl bridge.

L6 ANSWER 23 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1990:631584 CAPLUS

DN 113:231584

TI Manipulation of organolanthanide coordinative unsaturation. Synthesis, structures, structural dynamics, comparative reactivity, and comparative thermochemistry of dinuclear μ-hydrides and μ-alkyls with [μ-R₂Si(Me₄C₅)(C₅H₄)]₂ supporting ligation

AU Stern, David; Sabat, Michal; Marks, Tobin J.

CS Dep. Chem., Northwestern Univ., Evanston, IL, 60208, USA

SO Journal of the American Chemical Society (1990), 112(26), 9558-75

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

AB Lutetium and yttrium hydrocarbyl and hydride chemical based upon the chelating [R₂Si(η⁵-C₅H₄)(η⁵-Me₄C₅)]₂- ligand (R = Me, Et; abbreviated R₂SiCpCp") is described. The ligand is prepared by reaction of the corresponding R₂Si(Cp")Cl derivative with NaC₅H₅. Subsequent metalation and reaction with MCl₂·3THF (M = Y, Lu) yields R₂SiCpCp"MC₁₂ Li(OEt)₂ complex, which in turn can be alkylated to yield R₂SiCpCp"MC₁₂(TMS)₂ derivs. (TMS = SiMe₃). The x-ray crystal structure of Me₂SiCpCp"LuCH(TMS)₂ at -120° is of a bent-sandwich Cp'₂MX-type (Cp' = η⁵-Me₅C₅) with relaxed interligand nonbonded interactions vis-a-vis the Cp'₂M and Me₂SiCp"2M analogs [Lu-CH(TMS)₂ = 2.365(7) Å] and having one close Lu...MeSi [Lu-C = 2.820(8) Å] secondary interaction. These alkyls initiate the polymerization of ethylene and undergo relatively slow hydrogenolysis to yield dihydrides (R₂SiCpCp"MH)₂ via detectable intermediates of stoichiometry (R₂SiCpCp")₂M₂(H)(CHTMS)₂. The x-ray crystal structure of (Et₂SiCpCp"LuH)₂ at -120° has an idealized C₂h, Lu(μ-Et₂SiCpCp")₂(μ-H)₂Lu geometry with both bridging Et₂SiCpCp" and hydride ligands. These complexes react slowly (compared to monomeric Cp'₂MH and Me₂SiCp"2(MH), reversibly, and regiospecifically with α-olefins to form bridging alkyls of structure M(μ-R₂SiCpCp")₂(μ-H)(μ-R')M (R' = Et, Pr, hexyl). An x-ray crystal structure of Lu(μ-Et₂SiCpCp")₂(μ-H)(μ-Et)Lu at -120° shows the Lu(μ-Et₂SiCpCp")₂(μ-H)Lu framework is nearly identical with the dihydride above. The μ-Et fragment is bound very unsym. with Lu-C(α) = 2.46 (2) and 2.58 (2) Å. In addition, Lu-C(β) = 2.78 (2) Å suggests a strong secondary bonding interaction. Hydrogenolysis of the μ-alkyl linkages is considerably slower than for terminal alkyl bonds in Cp'₂M(alkyl) and Me₂SiCp"2M(alkyl) complexes. NMR studies of the M-alkyls reveal rapid rotation of the μ-alkyl ligands about the μ-H-μ-C(α) vectors down to -85° and rapid inversion at C(α) occurring with ΔG_{thermod.} = 12.5-13.6 kcal/mol (T_c = 11-39°). Kinetic (rate law: v = k [dihydride] [olefin]) and equilibration measurements reveal that the hydride addition process (Et₂SiCpCp"LuH)₂ + 1-hexene = Lu(μEt₂SiCpCp")₂(μ-H)(μ-hexyl)Lu is described by ΔH = -10.7 (6) kcal/mol, ΔD = -25 (92) eu, ΔH_{thermod.} = 12.0 (4) kcal/mol, and ΔS_{thermod.} = 38.6 (7) eu. These results indicate that, in comparison to terminal bonding modes with similar metal ancillary ligation, lanthanide μ-H ligands are kinetically deactivated with respect to olefin insertion (a rate depression of -108-1010), an μ-alkyl ligands are kinetically deactivated with respect to hydrogenolysis (a rate depression of -108-109). Moreover, relative to a bridging hydride ligand, lanthanide μ-alkyl coordination is no more and probably less thermodynamically stable than terminal alkyl coordination.

L6 ANSWER 24 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1986:5966 CAPLUS

DN 104:5966

TI Highly reactive organolanthanides. Synthesis, chemistry, and structures of 4f hydrocarbyls and hydrides with chelating bis(polymethylcyclopentadienyl) ligands

AU Jeske, Gerald; Schock, Laurel E.; Swebston, Paul N.; Schumann, Herbert; Marks, Tobin J.

CS Dep. Chem., Northwestern Univ., Evanston, IL, 60201, USA

SO Journal of the American Chemical Society (1985), 107(26), 8103-10

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CASREACT 104:5966

GI For diagram(s), see printed CA Issue.

AB MCl_3 ($M = Sm, Nd, Lu$) reacted with the silylbis(cyclopentadienyl) compound Li_2Cp_2 in THF to give $[Cp_2MCl_2][Li(OEt_2)_2]$ (I) following extraction with Et_2O . $NdCl_3$ and Li_2Cp_2 in THF gave the dimer II following extraction with pentane. The x-ray crystal structure of II showed $-Cl-$ and $-Cl-Li-Cl$ bridges between the 2 Nd atoms. I ($M = Sm, Nd, Lu$) reacted with $LiCH(SiMe_3)_2$ to give $Cp_2MCH(SiMe_3)_2$ (III). The x-ray crystal structure of III ($M = Nd$) showed the $CH(SiMe_3)_2$ fragments was coordinated to Nd in a highly unsym. fashion, with a Nd-C σ -bond and a secondary Nd-C interaction with a Si-bound C. III ($M = Sm, Nd, Lu$) reacted with H_2 to give the dimeric hydrides $Cp_2M(\mu-H)_2M Cp_2$, which are catalyst for ethylene polymerization, hexene-ethylene copolymer., and propylene oligomerization. Deprotonation of III ($M = Lu$) gave the lutetacyclobutane complex IV.

L6 ANSWER 25 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1984:551989 CAPLUS

DN 101:151989

TI Zirconocene- η^4 -1,3-pentadiene complex and its higher homologs. A new synthetic method involving σ - π rearrangement of the hydrido-2,4-pentadienylzirconium species

AU Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A.

CS Fac. Sci., Osaka Univ., Toyonaka, 560, Japan

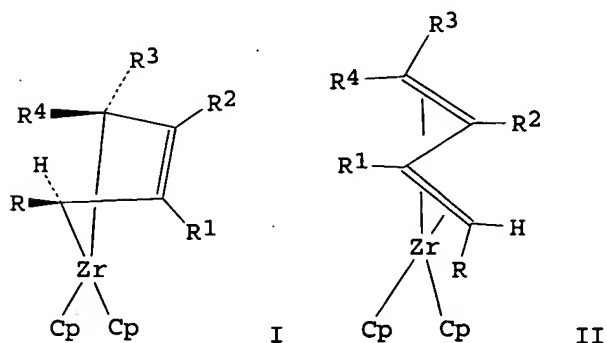
SO Organometallics (1984), 3(10), 1470-8

CODEN: ORGND7; ISSN: 0276-7333

DT Journal

LA English

GI



AB (Alkadiene)zirconocene complexes I and II ($Cp =$ cyclopentadienyl; $R = H, Me, SiMe_3$; $R_1, R_2, R_4 = H, Me$; $R_3 = Me, Et, CH_2SiMe_3$) were prepared by treating Cp_2ZrHCl with alkadienyl anions, via H transfer from Zr to the alkadiene. This was shown by the reaction of Cp_2ZrDCl and 2-methylpentadienyl K, giving I ($R = CH_2D$, $R_1 = R_3 = R_4 = H$; $R_2 = Me$). Both I and II ($R = H, Me$; $R_1 = R_2 = R_4 = H$; $R_3 = Me, Et$) occurred for 1,3-pentadiene and 2,4-hexadiene complexes but other alkadienes were single, cis isomers. $Cp_2Zr(2,4\text{-hexadiene})$ (III) reacted with $H_2C:CHPr$ or $H_2C:CH(CH_2)_4CH:CH_2$, CO, and acid with expulsion of the ligand and

formation of 3,4-dipropylcyclopentanone, or cis- and trans-hydrindanone, resp. Treating III with Me₂CHCHO and HCl gave aldehyde insertion and cleavage to form 72% R⁵CH:CHR⁵ [R⁵ = CHMeCH(OH)CHMe₂].

L6 ANSWER 26 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1984:174979 CAPLUS
DN 100:174979
TI Manipulation of organoactinide coordinative unsaturation and stereochemistry. Properties of chelating bis(polymethylcyclopentadienyl) hydrocarbyls and hydrides
AU Fendrick, Carol M.; Mintz, Eric A.; Schertz, Larry D.; Marks, Tobin J.
CS Dep. Chem., Northwestern Univ., Evanston, IL, 60201, USA
SO Organometallics (1984), 3(5), 819-21
CODEN: ORGND7; ISSN: 0276-7333
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB Lithiation and silylation of RH (R = tetramethylcyclopentadienyl) gave R₂SiCl₂, which was methylated to give the chelating ligand R₂SiMe₂. The last reacted with ThCl₄ to give cyclopentadienyl Th complex I (R₁ = Cl), which was alkylated to give the new, thermally stable thorium complexes I (R₁ = Bu, CH₂CMe₃, CH₂SiMe₃, CH₂Ph, Ph). The crystal structure of I (R₁ = CH₂SiMe₃) showed a small (ring center of gravity)-Th-(ring center of gravity) angle and a large ring-ring dihedral angle. I (R = Bu, CH₂CMe₃, CH₂SiMe₃, CH₂Ph, Ph) underwent facile hydrogenolysis to yield the new thorium hydride [(Me₂SiR₂)ThH₂]_x (II). The IR spectrum of II lacks terminal Th-H stretching transitions. II catalyzed 1-hexene, 2-hexene hydrogenation at turnover frequencies 13 and 21 times greater than (R₂ThH₂)₂ (R₂ = pentamethylcyclopentadienyl), resp.

L6 ANSWER 27 OF 27 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1981:550815 CAPLUS
DN 95:150815
TI Antitumor activity of metallocenes: ring-substituted and -bridged titanocene dichloride
AU Koepf-Maier, Petra; Kahl, Werner; Klouras, Nikolaos; Hermann, Gordian; Koepf, Hartmut
CS Inst. Anat., Freien Univ. Berlin, Berlin, D-1000/33, Fed. Rep. Ger.
SO European Journal of Medicinal Chemistry (1981), 16(3), 275-81
CODEN: EJMCAS; ISSN: 0009-4374
DT Journal
LA German
OS CASREACT 95:150815
AB Monosubstituted, 1,1'-disubstituted, and 1,1'-bridged titanocene dichlorides (RC₅H₄)(C₅H₅)TiCl₂ (R = Me, Et, SiMe₃), (RC₅H₄)₂TiCl₂ (R = Me, CMe₃, SiMe₃, SiMe₂Bu, GeMe₃), and Z(C₅H₄)₂TiCl₂ (Z = (CH₂)₃, CH₂, CHMe, SiHMe, SiEt₂, GeMe₂) were prepared by metalation of cyclopentadienes RC₅H₅ and Z(C₅H₅)₂ with BuLi followed by reaction with C₅H₅TiCl₃ or TiCl₄, resp. The resulting compds. as well as the indenyl and tetrahydroindenyl derivs. (C₉H₇)₂TiCl₂, (C₉H₁₁)₂TiCl₂, and (C₉H₁₁)(C₅H₅)TiCl₂ were investigated with regard to their antitumor activity against Ehrlich ascites tumor in mice. (EtC₅H₄)(C₅H₅)TiCl₂, (Me₃SiC₅H₄)(C₅H₅)TiCl₂, and (C₉H₁₁)(C₅H₅)TiCl, which are modified only at one cyclopentadienyl ring, show optimum cure rates of 80, 60, and 100%. Whereas these values are only slightly diminished in comparison to the unsubstituted titanocene dichloride, the tumor-inhibiting activity of complexes containing two modified C₅H₅ rings is strongly reduced. The weakening influence of chemical variation at the cyclopentadienyl rings on the tumor-inhibiting activity of metallocene dihalides is in agreement with the hypothesis of a carrier function of these five-membered ring ligands.

